OVERVIEW OF DEVELOPMENT IN CONTINUOUS EMISSIONS MONITORING FOR MIXED WASTE TREATMENT

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ABSTRACT

Waste treatment is an important application and market area for continuous emissions monitors (CEMs). In the mixed waste treatment area, for example, U.S. Department of Energy (DOE) has legal responsibility for treatment and disposal of a current inventory of more than one million cubic meters of low-level, high-level, and transuranic mixed waste. Future DOE decontamination, decommissioning, and environmental cleanup activities will likely bring the total to more than two million cubic meters. Thermal treatment processes such as vitrification, incineration, and plasma treatment will be employed for most of this waste, and all will be treated and disposed in compliance with applicable laws and regulations. CEMs will likely be required because of public concern and insistence that potentially hazardous emissions from the treatment processes be strictly limited, continuously monitored, and documented.

This paper provides an overview of the developing and envisioned regulatory and stakeholder situation with respect to CEMs and DOE waste treatment, and an overview of the status of currently available and emerging CEMs for particulate matter, Hg, multi-metals, dioxins / furans, and radionuclides. It provides technical descriptions of the technologies and performance information based on recent tests conducted under the auspices of the Mixed Waste Focus Area (MWFA), the Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP), and the U.S. EPA. It also identifies the CEM technology developers and describes the status and prospects of CEM development activities.

The primary goal is to acquaint potential CEM users with the availability and performance of CEMs for support of DOE waste treatment operations. A secondary goal is to stimulate thinking among both CEM developers and potential users on how to implement continuous monitoring, perhaps in combination with non-intrusive feed stream characterization and improved air pollution control, to help ensure safe and affordable treatment, proper performance, and public acceptance of thermal treatment facilities.

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DISCLAIMER

INTRODUCTION

Continuous emissions monitors (CEMs) can provide several benefits for mixed waste treatment. They can enable better control for safe, environmentally compliant operation of treatment facilities, provide documentation of such operation, and help provide greater assurance of the quality of the final waste forms. These benefits address important public concerns regarding the siting and operation of incinerators or other thermal treatment equipment. Hence, quality CEMs can improve public acceptance of such facilities.

Hazardous air pollutants (HAPs) are the emissions of concern for the CEMs addressed here. Congress has identified 189 HAPs [42 U.S. Code 7412]. They are regulated under the Clean Air Act and Amendments of 1990. The HAPs can be considered in three main classes: (1) hazardous organic compounds, (2) hazardous inorganics, and (3) radionuclides. Particulate matter (PM) is also of concern because it can be monitored fairly easily and because PM can serve as an indicator of the presence of HAPs.

For waste treatment processes such as incineration and vitrification, the organic emissions of greatest concern include chlorinated organic compounds such as the extremely toxic tetrachlorinated dibenzo-p-dioxins (TCDDs), dibenzofurans (TCDFs), and polychlorinated biphenyls (PCBs). The hazardous inorganic emissions of concern include gaseous inorganic pollutants such as CO, NO, NO_2, and SO_2, for which CEMs are required by regulation and are already widely used, and Cl_2, and HCl, which are addressed by the proposed MACT rule [EPA, 1996]. Other hazardous inorganic emissions that are already regulated include the so-called "heavy metals." These include the elements and compounds of two categories of metals: (1) the so-called MACT-rule metals and (2) other heavy metals classified as toxic by RCRA. The MACT-rule metals are Hg, the semi-volatile metals Cd and Pb, and the low volatility metals As, Be, and Cr. The other heavy metals, regulated under RCRA, are Ag, Sb, Ba, Co, Mn, Ni, Se, Tl, and V. The MACT-rule metals have that name because, according to the current EPA notice of proposed rulemaking [EPA, 1996], emissions of these metals from hazardous waste combustors will be regulated under the joint authority of the Clean Air Act and RCRA. Radionuclides, the final category of HAPs, are also a matter of concern for mixed waste treatment. Emissions of these materials are regulated under the Clean Air Act and DOE orders, and CEMs for radionuclides are desired for demonstration that treatment facilities are continuously operating in a safe and regulatory compliant manner.

Within the U. S. Department of Energy Office of Environmental Management (DOE EM), the Mixed Waste Focus Area (MWFA) and the Characterization, Monitoring and Sensor Technology Crosscutting Program (CMST-CP) are working together to provide CEMs to support safe, effective, and regulatory compliant mixed waste treatment and disposal. The MWFA is responsible for providing the right treatment technologies and the CMST-CP is charged with providing the necessary characterization and monitoring tools for such treatment. The two programs are working together on CEMs because, according to our best information, regulators will be treating DOE mixed waste thermal treatment facilities as hazardous waste incinerators. Furthermore, EPA has clearly stated its preference for CEMs as the preferred approach for ensuring regulatory compliance [EPA, 1996, page 17417]:

> *"The top tier of the compliance monitoring hierarchy is the use of a continuous emissions monitor system (CEMS) for that HAP or standard. In the absence of a CEMS for that HAP or standard, the second tier is the use of a CEM for a surrogate of that HAP or standard and, when necessary, setting some operating limits to account for the limitations of using surrogates. Lacking a CEMS for either, EPA sets appropriate feedstream and operating parameter limits to ensure compliance and requires periodic testing of the source."*

Particulate matter (PM) CEMs will be required when the MACT rule is promulgated; Hg CEMs will likely be required as soon as systems that meet EPA performance specifications are shown to be available. Also, although the MACT rule will not mandate multi-metals CEMS, it will most likely offer incentives for voluntary implementation. According to the proposed rule, the application of CEMs for hydrogen chloride (HCl), chlorine (Cl_2), mercury (Hg), semi-volatile metals (SVMs), and low-volatility metals (LVMs) can replace feedstream analysis for those components for regulatory compliance and remove them from consideration during required comprehensive and confirmatory tests. This is important for mixed waste because of the DOE ALARA requirement, i.e., to keep worker radiation exposure "as low as reasonably achievable" and because both the feedstream analyses and the testing, the latter comparable to the Resource Conservation and Recovery Act (RCRA) trial burn, are high cost activities. In addition, waste feed characterization, a RCRA requirement, can potentially be reduced significantly when CEMs are used. Also, the use of CEMs would eliminate the reliance on process operating parameters for regulatory compliance. For example, a facility would no longer use process operating parameters such as baghouse differential pressure, scrubber flow, or total offgas flow to show compliance with the particulate matter emission standard. Instead, a particulate matter CEM would verify continuous compliance with the standard, and waste feed cutoffs would no longer be tied to several process operating parameters.

Needs

The MWFA has performed thorough investigations of technologies available for mixed waste treatment, identified 30 technology deficiency areas, and prioritized those deficiencies with respect to their importance for achieving safe, effective, regulatory compliant, and affordable waste treatment [DOE, 1995, 1997]. The MWFA identified five deficiencies in the monitoring area: (1) Hg monitoring, (2) heavy metals monitoring, (3) alpha-emitting radionuclides monitoring, (4) volatile organic compounds monitoring, and (5) radionuclide distribution or monitoring. According to the MWFA, these deficiencies have nearly indistinguishable priorities in the range of 11 to 18 (1 is top priority).

Information concerning DOE EM technology needs was also gathered independently by the Site Technology Coordination Groups. According to these, valid methods for continuously monitoring mercury, heavy metals (Cd, Pb, As, Cr, and Be), and dioxins are needed to help ensure that emissions from MW thermal treatment facilities are maintained below permitted limits.

Teamwork

The CMST-CP and the MWFA began to work together on CEM activities in 1995; that teamwork continues today. In 1996 they formed an ad hoc CEM working group, which identified available monitoring technologies, assessed the technologies known to be under development, and identified technology gaps. In September 1996, they completed a draft CEM Technology Development Strategy document [French et al, 1996]. The strategy document, which is intended to be a dynamic entity, summarized the needs and opportunities and outlined a vision and proposed plans for how the CEM needs would be addressed.

One of the key products of the working group effort was a list of science and technology development projects that are applicable to process and emissions monitoring for mixed waste thermal treatment and were already funded by the federal government. The portion of the list that addresses the multi-metals CEM (MM CEM) portion of that work is given in Table I. Other projects address other process monitoring and CEM categories.

Table I. Federally funded projects related to multi-metals CEMs.

Development Project or Activity	**PI & Organization**	**Sponsor**
Acousto-optic tunable filter / Fabry Perot Interferometer (with DIAL air ICP-AES MMCEM)	David Baldwin, Ames Lab	CMST-CP
Real-Time On-line Measurement of Toxic Metal Emissions. Portable LIBS	Meng-Dawn Cheng, Oak Ridge National Laboratory	Strategic Environmental Research and Development Program (SERDP), up to three years beginning October 1996.
Microwave plasma analyzer MMCEM Development of an Ultra Sensitive Continuous Monitor for Mercury and Other Trace Metals in Flue Gas	Phillip Efthimion, EEI	EPA Small Business Innovation Research Program (SBIR) Phase II:
A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals	Scott Goode, University of South Carolina	DOE EM Science Program up to three years beginning 1996
LIBS MMCEM	David Hahn, Sandia National Laboratories, Livermore, California	CMST-CP & U.S. Army Armament Research, Development and Engineering Center
A Continuous Emission Monitor for Toxic Metals in the Off-Gases of Thermal Treatment Facilities	Gary Loge, Laser Diagnostics, LLC, Los Alamos, New Mexico	CMST-CP through the Federal Energy Technology Center (FETC)
Development of Cavity Ringdown Spectroscopy as a Sensitive Continuous Emission Monitor for Metals	George Miller, Mississippi State University	DOE EM Science Program, up to three years beginning 1997
Portable Sensor for Hazardous Waste (Active Nitrogen Energy Transfer & Spark Induced Breakdown Spectrometry)	Larry Piper, Physical Sciences Inc., Andover, Massachusetts	DOE EM Industry Programs (through FETC) for the Decontamination and Decommissioning Focus Area
LIBS MMCEM (J. P. Singh) and Air ICP-AES MMCEM (George Miller)	John Plodinec, DIAL Mississippi State University	DOE EM University Programs (for the MWFA)
ICP-AES MMCEM (Navy/TJA)	Mike Seltzer, U.S. Navy China Lake	U. S. Army Armament Research, Development and Engineering Center
Microwave Plasma Analyzer	Paul Woskov, MIT, Cambridge, Massachusetts	MWFA

The number of projects related to MM CEMs is impressive, and the total annual funding investment is in the millions of dollars. The number of federal programs providing funding for these projects, often with little communication with the other funding programs or offices, is equally impressive. Therefore, one obvious part of the strategy to accelerate the availability of the needed CEMs was to take advantage of the work funded by all these programs and to try to develop a single, coordinated technology development framework for the projects. Hence, the MWFA and the CMST-CP led in the formation of the Interagency CEM Technology Development Coordination

Committee and Working Group. These bodies convened for the first time in January 1997. The ICCC (shorthand for the Interagency CEM Coordination Committee) includes persons with funding authority and program direction authority for the projects of interest. The following organizations are represented: DOE-EM (MWFA and CMST-CP), DOE Office of Fossil Energy, EPA (Office of Solid Waste, the Office of Air Quality Planning and Standards, and Office of Research and Development), and Department of Defense (U.S. Army Demilitarization Technology Office, the U.S. Air Force, and the Strategic Environmental Research and Development Program (SERDP)). The ICCC meets only once or twice a year, but is supported by the Interagency CEM Technology Development Working Group. The latter provides information and recommendations to the ICCC. The principal purpose of both groups is to coordinate their activities in a way that accelerates CEM development, validation, and application. The principal collaborative activities undertaken so far are: (1) promotion of information sharing at the sponsor and principal investigator levels, and (2) collaboration in conducting quantitative evaluations of the performance of CEMs in realistic test environments.

CEM PERFORMANCE TESTING

CEM performance tests are important to regulators, instrument developers, and potential CEM users. EPA has published draft performance specifications (requirements) for CEMs [EPA, 1996b, 1996c, 1996d]. Instruments that satisfy the PS can be used to fulfill CEM requirements or to take advantage of incentives addressed in regulations; instruments that don't satisfy the EPA PS don't have regulatory value. Developers and users need test results to see how the various competing CEMs perform under realistic operating or test conditions. The test results help guide development and application decisions.

DOE (MWFA and CMST-CP) and EPA have collaborated in conducting several CEMs performance tests pertinent to MW thermal treatment. The tests are listed below; summary descriptions of the tests and their results are provided in succeeding portions of this paper.

- DOE / EPA CEMs Performance Test at the EPA Incineration Research Facility, August and September 1995
- Extended Duration Particulate Matter (PM) CEMs Testing, September 1996 through May 1997
- Extended Duration Hg CEMs Testing, December 1996 through May 1997
- DOE/EPA Multi-Metal CEM Test at the EPA Rotary Kiln Incinerator Simulator, April 1996
- Bench-Scale Jet-REMPI / TOFMS Dioxin CEM Feasibility Test, September and October 1996
- Multi-Metals CEMs Test at the DOE Oak Ridge TSCA Incinerator, September 1997
- DOE/EPA Multi-Metals CEMs Test at the EPA Rotary Kiln Incinerator Simulator, September 1997

The following approach was used for all the tests: The flue gas was spiked to provide pollutant concentrations near the EPA emission limits. The CEMs were used to analyze the flue gas while the concentrations were also simultaneously measured using conventional, laboratory-based EPA Reference Methods. The performance of the CEMs was measured both in comparison to the results obtained by the EPA reference methods and in comparison to draft performance specifications (PS) proposed by the EPA [EPA, 1996b, 1996c, 1996d].

The key elements of the draft PS for multi-metals CEMs are given below, for example.

- Sampling must be continuous
- Relative Accuracy (RA) ≤ 20% (It is generally accepted that this means the detection limit must be ≤ 10% of the Emission Limit for the metals of concern.)
- Measure all pollutants (i.e., all six MACT metals)
- Response Time ≤ 2 minutes (In real systems it is not possible to measure this unless a calibration gas or equivalent is available.)
- Instrument Availability ≥ 95%
- CEM Calibration Drift ≤ 10% of Emission Limit
- Zero Drift (ZD) ≤ 5% of Emission Limit
- Interference Response ≤ 10% of Emission Limit (This specification pertains to a Hg CEM; a similar specification would be reasonable for a multi-metals CEM.)

DOE / EPA CEMs Performance Test at the EPA Incineration Research Facility, August, September 1995.
In two separate test periods in August and September 1995, DOE and EPA jointly conducted one-week tests of 11 CEMs at the EPA Incineration Research Facility (IRF) in Jefferson Arkansas. The IRF was a pilot scale rotary kiln incinerator with a wet air pollution control system. The CEMs included four Hg CEMs, two multi-metals CEMs, four volatile organic compounds CEMs, and one semi-volatile organics CEM. A detailed description of the IRF tests and results has been published [Ghorishi et al, 1996]. Some key overall results can be summarized as follows:

- Because of the flue gas moisture, particulate loading, and interferences, all the CEMs had difficulty with real flue gas.
- The multi-metals CEMs exhibited poor detection limits and Relative Accuracy for most metals.
- The Hg CEMs were at a more advanced state of development than the other CEMS.
- More field-testing will be required for all the other CEMs.
- None of the CEMs satisfied proposed EPA performance specifications.

Extended Duration Particulate Matter (PM) CEMs Testing, September 1996 through May 1997.
During this period, EPA and DOE conducted extended duration testing of PM CEMs at the DuPont Experimental Station hazardous waste incinerator located in Wilmington, Delaware. The purpose was to determine what commercially available PM CEMs could meet the EPA draft performance specification (PS11) and calibration statistical data quality objectives [EPA, 1996c] under actual field use conditions. Five PM CEMs were tested:

- Verewa F904-kD, beta type
- Durag Dr300, light-scattering type
- Emissions SA Beta 5M, beta type
- Environmental Systems Corp. Model P5A, light-scattering type
- Sigrist ktNR, light-scattering type

The air pollution control system at the DuPont facility included a spray dryer, venturi scrubber, spray absorber, and an electrodynamic venturi. The flue gas conditions were:

Temperature:	285-325°F	Moisture:	16-30%
Velocity:	10-12 m/s	PM Loading:	5-100 mg/dscm

The test procedure and findings have been described in a draft report [EPA, 1997]. The key findings from the extended duration PM CEMs testing at DuPont were:

- The five PM CEMs operated for 9 months; 100 pairs of EPA Method 5 and PM CEM data were obtained.
- All five PM CEMS achieved PS11 calibration statistical data quality objectives for correlation coefficient, confidence interval, and tolerance interval.
- Four PM CEMs satisfied the PS11 data availability requirement.
- PM CEMs of both beta, and light-scattering types were able to satisfy the draft PS11.
- The PM CEM results exhibited reproducibility equal to those from the EPA Reference Method.

Extended Duration Hg CEMs Testing, December 1996 through May 1997
During this period, DOE and EPA conducted extended duration testing of Hg CEMs at the Holnam Inc. cement kiln located in Holly Hill, South Carolina. The purpose was to determine what commercially available Hg CEMs could meet the EPA draft performance specification (PS12) and calibration statistical data quality objectives [EPA, 1996d] under actual field use conditions. Three monitors were tested:

- Verewa, HM-1400
- Seefelder Messtechnik Hg-Mat 2
- Perkin-Elmer MERCEM

The Holnam Inc. facility was equipped with an electrostatic precipitator; the flue gas conditions were as follows:

Temperature:	355°F	SO2	100-1000 ppm
Velocity:	15-20 m/s	NO2	50-500 ppm
Moisture:	35%	Hg emissions:	15-30 μg/dscm

The key findings from the extended duration Hg CEMs testing were:

- None of the tested Hg CEMs met the EPA draft performance specification (PS12).
- The Hg CEMs measured total Hg. They did not distinguish between elemental mercury and mercuric chloride (although the Hg PS doesn't require such distinction). Detection of particulate-bound Hg was not demonstrated.

- The Hg CEMs had maintenance difficulties caused by condensible acid gases and particulate matter. They also suffered significant interference effects at high SO_2 concentrations (500 ppm). These problems suggest that the flue gas sampling and sample conditioning arrangements need improvement.
- Improved calibration sources are needed to reliably evaluate CEM performance. That is, reference materials with known, repeatable concentrations are needed to reliably measure calibration drift, accuracy, and linearity

DOE/EPA Multi-Metal CEMs Test at the EPA Rotary Kiln Incinerator Simulator, April 1996
In April 1996 DOE and EPA conducted a one week test of multi-metals CEMs at the EPA rotary kiln incinerator simulator, Research Triangle Park, North Carolina. The principal goal of the test was to determine the Relative Accuracy of the CEM results as compared to EPA Method 0060 (Method 29). Three CEMs were tested:

- A laser-induced breakdown spectroscopy (LIBS) CEM prototype from the Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University
- A second LIBS CEM prototype, from Sandia National Laboratories, Livermore, California, and
- An inductively coupled plasma atomic emission spectroscopy (ICP-AES) system provided by a U.S. Navy China Lake and Thermo Jarrell Ash (TJA) team.

Information concerning this test and its results has been also been published [Haas et al, 1997]. At the concentrations tested, the Navy/TJA ICP-AES system measured all seven test metals; the LIBS systems measured only one to four metals. The Navy/TJA system achieved 50 to 100% Relative Accuracy levels – better than the other CEMs but not good enough to meet the draft EPA PS [EPA, 1996b]. The detection limits need improvement for all these CEMs. The Navy/TJA system needs improvement for Hg; the LIBS instruments need detection limit improvement for all seven metals. As configured for this test, i.e., with only one spectrometer each, neither of the LIBS instruments could simultaneously observe the desired spectral lines for all seven of the target metals. As a result, for any given metal, the LIBS systems typically recorded data for only about 30% of each RM measurement period. The Navy/TJA system, on the other hand, was able to observe all seven of the target metals simultaneously. Response times for all the instruments, to the extent they could be estimated, appeared to satisfy the draft PS.

Bench-Scale Jet-REMPI / TOFMS Dioxin CEM Feasibility Test
In September and October 1996 DOE and EPA collaborated in conducting bench scale feasibility testing of an innovative system for real-time detection of dioxins [French et al, 1997]. The Jet-REMPI / TOFMS system, provided by DLR Stuttgart, uses a pulsed tunable laser to selectively ionize jet-cooled molecules found in the flue gas by resonance enhanced multi-photon ionization (REMPI) and then detects the ionization products by time-of-flight mass spectrometry (TOFMS). The tests were conducted at the EPA National Risk Management Research Laboratory, Research Triangle Park, North Carolina, The tests employed a gas chromatography system to generate known concentrations of pure mono- through tetra-chlorinated dioxins for examination by the Jet-REMPI / TOFMS system.

The tests provided the first real-time measurement of dioxins in simulated flue gas (air) – with a detection limit of 30 ng/m^3 for 2, 7 dichlorodibenzo-p-dioxin. Detection limits for the tetrachlorinated dibenzo-p-dioxins were estimated to be approximately 1000 ng/m^3, three to six orders of magnitude greater than what would be required for a dioxin CEM capable of measuring dioxins at levels near the proposed emission limit. Hence, one conclusion of the test was that sample preconcentration and particle – gas separation, both without impact on the dioxin/furan chemistry, will be necessary and crucial parts of any successful dioxin/furan CEM approach. The positive test results also reinforced EPA interest in a dioxin CEM. Today, Jet-REMPI/TOFMS is viewed as one potentially successful CEM approach. Other approaches under consideration include fast gas chromatography with mass spectrometer detection and gas chromatography with surface acoustic wave sensor detection. The ultimate goal is good dioxin control and documentation of the same. Therefore, because dioxin detection requirements are so challenging, it will be important in future dioxin CEM development to closely coordinate that development with identification of dioxin formation mechanisms, precursors, measurement surrogates, and control strategies – all with the goal of identifying things that are easier to measure than dioxins but accurately indicate toxicity attributable to dioxins.

Multi-Metals CEMs Test at the DOE Oak Ridge TSCA Incinerator (TSCAI), September 1997
The purpose of this test was to investigate the deployment potential of three multi-metals monitoring systems under TSCAI stack conditions and, based on the findings, to make recommendations concerning future testing, evaluation, and/or deployment of a metals monitor. Three multi-metals monitoring systems were tested:

- Hazardous Element Sampling Train (HEST) provided by Cooper Environmental Services, Beaverton, Oregon;
- A LIBS system provided by Sandia National Laboratories, Livermore, California, and
- An inductively coupled plasma atomic emission spectrometry system (TraceAIR ICP-AES) provided by a Thermo Jarrell Ash (TJA) and U.S. Navy China Lake team.

The TSCAI was operated with radioactive organic liquid and aqueous waste feeds. The air pollution control system included a water quench, venturi scrubber, packed bed scrubber, and two stages of ionizing wet scrubber. The flue gas conditions were:

Temperature:	180°F	Particulate:	0.01-0.03 gr/dscf
Velocity:	6 m/s	SO_2	1 ppm
Moisture:	50% (saturated)	NO_2	60-80 ppm

The test considered the performance of the monitoring systems for the MACT rule elements, As, Be, Cd, Cr, Pb, and Hg, and for other elements known to be present in the test waste, Sb, Ba, Co, Mn, Ni, Se, Ag, Tl, and U. Most of these latter elements will potentially be regulated under RCRA in the new TSCAI permit. The feed was spiked with As, Cd, Cr, Pb, and Hg at three test levels (low, medium, and high). The target concentrations of these MACT rule elements in the flue gas were 10, 100, and 500 μg/dscm. Measurements made by the monitoring systems were compared with those obtained from samples collected concurrently using EPA Reference Method 29 (multi-metals sampling train). Six Method 29 runs were collected at each of the three target concentration levels. The Method 29 samples were analyzed on site using EPA SW-846 methods 6010b and 6020. The HEST filter samples were also analyzed on site, using wavelength dispersive X-ray fluorescence spectrometry.

The TSCAI test team prepared special criteria for evaluation of the deployment potential of the test monitoring techniques at the TSCAI. The principal criteria focused on two questions:

1. Did the monitoring results meet the EPA PS-10 Relative Accuracy specification (RA < 20%)?
2. Did the monitoring results satisfy alternative bias (relative to RM29), and precision criteria?

The purpose of the second, less demanding, set of criteria was to discount the effects of the RM imprecision, if any. Additional criteria considered uptime, response time, calibration and check procedures, and automation.

The Relative Accuracy results are presented and summarized using a scoring method in Table II.

Some of the highlights of the TSCAI test findings are as follows:

- The TraceAIR system experienced problems with water condensation in the sampling interface and the ICP torch and nebulizer areas.
- With one exception (HEST RA of 19% for medium-level chromium-spiked runs), none of the monitoring techniques met the EPA draft PS-10 Relative Accuracy specification for any of the test elements.
- Of the 6 MACT rule elements for which data was requested, the TraceAIR CEM reported data for 6, the LIBS CEM reported data for 5 (all but As), and the HEST technique reported data for 5 (all but Be).
- Of the 15 elements for which data was requested, the TraceAIR CEM reported data for 8 elements, the LIBS CEM reported data for 6 elements, and the HEST technique reported data for 9 elements.
- The HEST technique, although not a CEM technique as implemented in this test (because the X-ray fluorescence analyses of the material collected on the HEST filters were performed off line), provided RA results that were consistently better than those of the TraceAIR and LIBS CEMs. This is evidenced by the scores shown in Table II.

Many additional findings and conclusions, particularly with respect to the evaluation of deployment potential at TSCAI and the additional criteria mentioned above, are contained in the draft test report [Dunn et al, 1998]. We are grateful to Dr. Dunn and coworkers for providing early access to the test results.

Table II. Relative Accuracy results from the TSCA incinerator test[a].

	Relative Accuracy (%)	**Score[b]**	**Relative Accuracy (%)**	**Score[b]**	**Relative Accuracy (%)**	**Score[b]**
	TraceAIR	**TraceAIR**	**LIBS**	**LIBS**	**HEST**	**HEST**
As – Low Level	162	2	NR	0	114	3
As – Medium Level	365	2		0	67.5	3
As – High Level	109	2	NR	0	64.5	3
Be	4880	2	154	3	NR	0
Cd – Low Level	97.2	2	624	1	46.5	3
Cd – Medium Level	507	1	70.6	2	44.0	3
Cd – High Level	176	1	91.6	2	30.1	3
Cr – Low Level	172	2	928	1	109	3
Cr – Medium Level	475	1	23.3	2	19.0	3
Cr – High Level	66.1	1	45.6	2	90.9	3
Pb – Low Level	88.5	2	379	1	25.8	3
Pb – Medium Level	511	1	136	2	45.3	3
Pb – High Level	127	1	108	2	39.8	3
Hg – Low Level	151	2	631	1	127	3
Hg – Medium Level	960	1	355	2	35.6	3
Hg – High Level	683	1	102	2	76.7	3
Subtotal score for MACT elements		**24 of 48**		**23 of 48**		**45 of 48**
Sb	NR	0	NR	0	NR	0
Ba	57.9	3	NR	0	NR	0
Co	NR	0	NR	0	173	3
Mn	NR	0	291	2	234	3
Ni	3670	2	NR	0	48.0	3
Se	NR	0	NR	0	NR	0
Ag	NR	0	NR	0	NR	0
Tl	NR	0	NR	0	NR	0
U	NR	0	NR	0	22.2	3
Subtotal score for other elements		**5 of 27**		**2 of 27**		**12 of 27**
Grand total score for all elements tested		**29 of 75**		**25 of 75**		**57 of 75**

[a] NR = Not reported
[b] Score = 3 for best RA, 2 for next best, 1 for third best; 0 for NR.

DOE/EPA Multi-Metals CEMs Test at EPA Rotary Kiln Incinerator Simulator, September 1997

In this second one-week test at the EPA RKIS, the performance of nine MM monitoring techniques was evaluated:

- Two ICP/AES systems, one provided by the U.S. Navy China Lake and Thermo Jarrell Ash team; one provided by the Diagnostic Instrumentation and Analysis Laboratory (DIAL), Mississippi State University (MSU)
- Two LIBS systems, one provided by Sandia National Laboratories, Livermore, California, ; one provided by DIAL MSU
- A Spark Induced Breakdown Spectroscopy provided by Physical Sciences Inc., Andover, Massachusetts
- A Microwave Induced Breakdown Spectroscopy system provided by Massachusetts Institute of Technology, Cambridge, Massachusetts
- A Hazardous Element Sampling Train (HEST) (with off site X-ray fluorescence analysis of the filters) provided by Cooper Environmental Services, Beaverton, Oregon

In addition, Laser Diagnostics, Los Alamos, New Mexico, performed special post-processing of some LIBS data obtained from the Sandia instrument. Also, DIAL and Ames Laboratory investigators collaborated to apply a high resolution interferometric spectrometer (HiRIS) for measurement of emission signals from the DIAL air ICP.

The principal findings from the September 1997 MM monitoring tests were:

- Only the Navy/TJA ICP-AES CEM measured all 6 of the MACT target elements in real time.
- The DIAL ICP monochromator-based CEM measured 5 (all but As), the HEST monitoring technique measured 5 (all but Be), and the DIAL LIBS system measured 4 (all but As and Hg).
- None of the tested systems met the draft EPA performance specification requirement for Relative Accuracies of 20% or less. For the four systems mentioned just above, the Relative Accuracies for the high concentrations were fairly similar. They ranged from 20 to 95% depending upon the element and system. For all systems, the range was 20 to 340%.
- The CEM results exhibited rather large variability – standard deviations as large as 50%, even for data points obtained by time averaging over periods as large as 90 seconds. Consequently, depending on the time interval finally designated for compliance /control monitoring, data variability may be an important performance parameter.

These and other findings, conclusions, and recommendations are described in French et al, 1998.

Radionuclides CEMs

The need for a radionuclides CEM is unique to DOE. Radionuclide emissions are regulated under DOE orders and the Clean Air Act National Emission Standards for Hazardous Air Pollutants (NESHAPS). The regulation is risk based, limiting the exposure of a maximally exposed individual at the site boundary or beyond to no more than 10 mrem/year. As a result, a model is required to translate from that maximum exposure level to equivalent stack gas concentrations. An assessment of the levels of radionuclides that might be emitted from mixed waste thermal treatment facilities using multiple High Efficiency Particulate Air (HEPA) filters has been performed [French et al, 1996]. These calculations indicate that such facilities will emit extremely low levels of radionuclides. Based on those calculations and the sensitivity required to conduct continuous monitoring at levels near the emission limit, it appears currently available and emerging radionuclide monitors have insufficient detection capability for CEM use if measurement cycle times must be as short as the two minute response time EPA has proposed in the draft performance specification for multi-metals CEMs.

Current activities in the radionuclides CEM area include (1) testing a commercially available monitor (EG&G Berthold) at Oak Ridge National Laboratory, and (2) efforts to deploy a near-real-time alpha CEM (developed at Los Alamos National Laboratory) at the Oak Ridge TSCA incinerator. The Berthold monitor operates by sampling and analysis. Depending upon the sample time, one can achieve very good sensitivity (detection limits) at the expense of real-time monitoring capability. A typical sampling time is about one hour. The Los Alamos instrument, known as a flow through alpha monitor (FTAM), is capable of an analysis in as little as 15 seconds, but with less sensitivity than the Berthold. Both these monitors depend on counting disintegrations, so sensitivity depends on the length of time over which the measurement is made. When the sampling and counting times for the Berthold and FTAM instruments are comparable they have comparable sensitivity. Potential advantages of the FTAM over the Berthold instrument are tolerance to saturated water vapor and somewhat higher temperature, and the ability to measure the entire stack gas flow rather than only an extracted sample. The principal advantage of the Berthold monitor is its commercial availability.

Status of PM, Hg, Multi-Metals, and Radionuclides CEMs

Of the CEMs addressed in this paper, only PM CEMs have been shown to meet the proposed EPA performance specifications. Based on the results of the recently completed extended duration testing, Hg CEMs are close but have not been demonstrated to meet EPA performance specifications. The Hg CEMs do appear to have sufficient detecting power to make useful measurements at levels near the emission limit. However, their gas sampling and conditioning arrangements have problems with particulates, acid gases, and moisture, and are consequently unreliable. HCl/Cl_2 CEMs are commercially available, however EPA has not yet validated their performance. No multi-metals CEMs that meet the performance specification proposed by EPA are available. The ICP-AES system advanced by the U.S. Navy / Thermo Jarrell Ash team has shown the ability to monitor all the MACT metals. In addition, it has come close, but has not yet achieved Relative Accuracy performance that satisfies the proposed EPA PS. (There is, in fact, some question whether an additional set of independent EPA reference method measurements would meet the requirement for Relative Accuracy $\leq$ 20%.) In the case of radionuclides, the available and emerging systems do appear to have sufficient detection power to monitor flue gas radionuclide emissions at levels corresponding to NESHAPS limits, but only for measurement and reporting periods of one hour or longer. Shorter measurement and reporting intervals are supported by these instruments, but then sensitivities decrease to the point where only emission levels much larger than the emission limit can be detected. In that mode the radionuclide CEM could function as an alarm – notifying the facility operator and the public that something had gone wrong and that emission limits for radionuclides had been exceeded.

CEM NEEDS AND PATH FORWARD

CEM Needs

Improved sampling and sample conditioning systems are needed for Hg CEMs. When such systems are provided, the present, commercially available Hg CEMs will likely be able to meet the proposed EPA PS. In the case of the MM CEMs, improved Relative Accuracy is needed. Generally, because Relative Accuracy is poorest at concentration levels approaching the limits of detection, this means improved power of detection is required. At this time, the deficiencies in RA and powers of detection seem to be more important for the CEMs that employ lasers and fiber optics (LIBS, SIBS) than for those that do not (ICP-AES).

The lack of field calibration systems and procedures is an important deficiency for Hg CEMs and most of the MM CEMs. Such systems and procedures are essential for performing the calibration checks required in the PS. More important, however, valid calibrations are essential for accuracy in the concentration measurements. Because the calibrations embody the relationships between the actual analyte concentrations and all the instrumental and sample matrix parameters that impact the measured concentrations, and because those parameters cannot be warranted as constant, we must have accurate calibrations to begin with and they must be updated from time to time under actual operating conditions. For CO and O_2 CEMs, the availability and use of "calibration gas" from a pressurized cylinder satisfies field calibration requirements. Permeation tubes that release Hg at a constant, known rate under certain fixed temperature and pressure conditions have been developed for use in the laboratory. However, these systems are not well suited for use in the field. Reliable delivery of known concentrations of Hg in the field at levels near the emission limit is very difficult, in part because, at those levels, Hg appears to be absorbed by materials that are ordinarily considered inert [Roberts et al, 1996].

A lower cost way of validating MM CEM performance is also desired. The current way – comparison to the results of EPA reference methods that employ flue gas sampling and analysis in an off-site analytical laboratory – is too expensive.

Extended duration tests of PM and Hg CEMs have been conducted; the operations of these systems appear to be sufficiently automated. The same is not yet true for the MM CEMs. At present, the operation of these systems appears to require almost constant attention from a human operator. To succeed in commercial or regulatory compliance monitoring these systems will require automation to reduce their dependence on personnel for routine operational activities including quality assurance activities and data management and reporting operations. A variety of CEM costs will be important. The capital, operating, and maintenance costs will all have to be balanced against the benefits of CEM application.

Path Forward

We think the priority actions listed below make sense in light of DOE EM and EPA objectives and what we have learned from the performance tests.

- Promote improvement of sampling / sample conditioning for Hg CEMs -- then validation testing;
- Promote improvement of detection capability and Relative Accuracy for MM CEMs -- then validation testing;
- Update the CEM technology development strategy document, especially regarding dioxins and fine particulate matter, both topics of high and increasing regulatory concern;
- In partnership with EPA, develop and implement an integrated dioxin control and monitoring strategy;
- Develop improved understandings of the rationale and procedures for key elements of the proposed performance specifications for MM CEMs, e.g., Relative Accuracy, measurement cycle time for compliance / control monitoring, data variability.

We intend to work further on these ideas and plans with the Interagency CEM Technology Development Working Group. We also intend to get input and generate support from the Interagency CEM Technology Development Coordination Committee. In the meantime, we present them here for consideration.

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